Mechanical Properties and Structure of Deformed and Subsequent Heat-treated Co-Ni-based Alloy with Medium Stacking Fault Energy

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論文内容要旨

This study was performed to elucidate the enhancement mechanisms of Co-32%Ni-20%Cr-10%Mo alloy (CNCM) in practical use. This alloy has been applied as spring material of precision machines because of its high elastic modulus, strength and fatigue resistance under high cyclic stress. Young's modulus is generally known to depend on both the material and the crystal orientation. However, the effect of dislocation inelasticity on Young's modulus has not been clarified. Experimental results of the present study suggest that dislocation inelasticity is a factor which should be considered to affect Young's modulus. Additionally, the strengthening due to the Suzuki effect is effective in CNCM while enhancement mechanisms such as precipitation hardening and martenstic transformation are known to be general enhancing mechanisms. This is because CNCM has a stable FCC structure at room temperature and hardly precipitates second phases. The Suzuki effect is considered to appear markedly in CNCM because stacking faults developed during heat treatment as compared with other practical use alloys exhibiting the Suzuki effect, which enables dislocations to be strongly locked. The stacking fault bounded by partial dislocations has often been reported when the Suzuki effect occurs. That is, the controlling dislocation structures in CNCM are suggested to enhance the mechanical properties.

Furthermore, texture formation during cold rolling was investigated because a spring is formed from CNCM through cold rolling. Generally, plastic deformation forms the preferred crystal orientation, the so-called texture. Most rolled alloys tend to exhibit texture transition after recrystallization. However, little attention has been paid to texture formation through deformation and recrystallization. In this study, the relation between dislocation structure and the mechanical properties of CNCM was investigated through cold rolling and subsequent heat treatment. The main results can be summarized as follows.

The deformation behavior of FCC alloys generally depends on stacking fault energy (SFE). SFE is an interfacial energy which determines the width of dissociated dislocations, such width affecting the dislocation motion such as climbing and cross-slips. CNCM has a stable FCC single phase at room temperature, which has SFE of 13-15 mJ/m^2 from the calculation based on the thermodynamic model and measurement by the X-ray diffraction technique. The rolling texture of CNCM was different from that of usual low SFE alloys though CNCM can be classified as a so-called low SFE alloy. The difference was revealed by comparison with Co-35Ni alloy having almost the same SFE as CNCM. The Goss component {110}<001> was a major texture component in cold-rolled CNCM, while in Co-35Ni, The Brass component {110}<112>, which generally appears in low SFE alloys, was observed. Furthermore, the dislocation density of CNCM, which was measured by the XRD technique, kept increasing during deformation and reached 4.5×10^{16} m^{-2} after cold rolling to 90% reduction. On the other hand, in Co-35Ni, the dislocation density increased greatly before cold rolling to 50% reduction, and slowly reached approximately 7.7×10^{15} m^{-2} after 90% cold rolling. Because CNCM contains solute atoms such as Mo and Nb to bind dislocations, the dislocations were easily accumulated as compared with Co-35Ni. Therefore, the deformation behavior of CNCM cannot be explained only by SFE.

Static recrystallization behavior is known to generally proceed with nucleation during recovery and the growth. The general recrystallization can be explained as being due to discontinuous recrystallization with changing the texture. CNCM after 70% cold rolling recrystalized without changing the texture, or the deformation texture remained even after complete recrystallization. In addition, a mean grain size of 2 μm was obtained through conventional cold rolling and annealing. Accordingly, CNCM can be considered to recrystallize in a continuous manner. The grains contain stacking faults bounded by partial dislocations at the beginning of annealing, indicating that the Suzuki effect occurs. With a further increase of annealing time, perfect rather than partial dislocations were observed in the grains at the beginning of heat treatment. The change of dislocation morphology indicates that microstructure evolution proceeds mainly due to recovery. The Suzuki effect is regarded as a key factor for continuous recrystallization in CNCM.

Young's modulus is difficult to increase by processing only because the value depends on the materials. Some attempts have been made to enhance Young's modulus. For example, texture control is regarded to be effective because the elastic constant depends on the crystal orientation. Texture transition was not observed in highly strained CNCM even after recrystallization because of the continuous manner. Nevertheless, the Young's modulus of CNCM after heat treatment increased to 13% as compared with that before the treatment. At this time, the strength also was improved, which is considered to be due to the Suzuki effect. The enhancement mechanism of CNCM has been suggested to be due to the Suzuki effect. Young's modulus can decrease when dislocations bow out in the material. When the Suzuki effect occurs, dislocation is strongly locked. Accordingly, the increase in Young's modulus is attributable to dislocation-locking due to the Suzuki effect.

The Suzuki effect is considered to be a characteristic phenomenon of CNCM. The dislocation structure with stacking faults has been observed and the effect has been reported to improve the strength. However, the dislocation structure and mechanical properties are related, and furthermore, the stacking faults are strongly locked, resulting in an increase of strength. This observation regarding the stacking faults is insufficient to relate the Suzuki effect to the dislocation locking mechanism. Therefore, dislocation locking was analyzed to investigate the amplitude dependence of internal friction. The internal friction is caused by the dispersion of external stress due to bowing out of the dislocation. The amplitude dependence of internal friction of CNCM disappeared after aging heat treatment, indicating that dislocations cannot bow out. From the analysis based on Granato-Lucke theory, the distance between pinning points decreased in CNCM after aging heat treatment. TEM observation indicated that the aged CNCM contained many stacking faults. Furthermore, stacking fault probability after aging of CNCM increased 7 times as compared with that before aging, as estimated by the XRD technique. Thereby, dislocation is continuously locked along the entire line length by the Suzuki effect, denoted the "Continuous locking mechanism". This locking mechanism is considered to be different from Cottrell's effect caused by local locking. An interesting question is how long the strong locking mechanism can be maintained.

Thermal stability of CNCM after strong cold-rolling was investigated by heat treatment at 700℃ for a maximum of 72 h. The temperature has been considered to exhibit the Suzuki effect because CNCM aged at that temperature is markedly strengthened. From the XRD technique, the dislocation density was kept at a high value of 10^{15} m^{-2}, even after holding for 72 h. Numerous stacking faults indicating the Suzuki effect were observed in aged samples. The Suzuki effect is considered to contribute to suppression of the thermal evolution of the microstructure. However, the density of dissociated dislocations tends to decrease with the precipitation of $(Co, Ni)_3(Mo, Nb)$ at the grain boundaries. Instead, perfect dislocations were observed. That is, the deformed CNCM recovered due to weakening of the Suzuki effect.

CNCM can be strengthened by applying strain aging heat treatment. Such strengthening is different from the common age hardening by local pinning of dislocations. The chemical interaction between a dislocation and solute atoms, the so-called Suzuki effect, is considered to mainly be responsible for the locking mechanism. The dislocations in CNCM cannot move after aging heat treatment because of continuous locking. Climbing motion is difficult for the locked dislocations, while the locally pinned dislocations overcome the obstacles with thermal activation. The difference of thermal stability of the deformed structure causes the characteristic recrystallization behavior. The deformed CNCM recrystallizes with recovery at the same time in a continuous behavior at lower rolling reduction compared with other materials exhibiting continuous recrystallization. Therefore, the grain size of CNCM can be controlled without texture transition due to recrystallization. Additionally, the Suzuki effect causes Young's modulus and strength to improve simultaneously. These findings are expected to lead to a quick-impact method of improving mechanical properties of CNCM.

論文審査結果の要旨

本論文はCo-Ni-Cr-Mo合金（以下、CNCM）の機械的特性の向上を目標として、冷間加工後とその後の熱処理による機械的特性の組織学的因子を体系的に検討している。

本論文は8章で構成されている。

第1章「Introduction」では、Co基合金におけるCo-Ni-Cr-Mo合金の位置づけを示し、代表的な研究報告を整理し、さらに機械的特性の向上のための方針を記述している。

第2章「Deformation behavior of Co-Ni-based alloys」では、冷間圧延による組織の変化を集合組織およびX線ラインプロファイル解析で転位密度を測定し明らかにしている。圧下率90％の冷間圧延後の集合組織は変形双晶に起因し、Goss方位が主方位であることを結晶学的に説明した。また90％冷延をしたCNCMの転位密度は4.5×10^{16} m^{-2}であり、溶質原子の作用で転位が蓄積しやすいことを示している。

第3章「Recrystallization behavior of Co-Ni-based alloys」では、圧下率70％以上の冷間圧延したCNCMは再結晶後の集合組織が加工集合組織と同様であること、静的再結晶にもかかわらず2μmの平均結晶粒径であること、組織の熱的変化が回復で進行することから再結晶挙動が連続再結晶であることを示した。

第4章「Young's modulus and strength of CNCM after aging heat treatment」では、スウェージ加工したCNCMのひずみ時効熱処理による高ヤング率化、高強度化を検討している。CNCMでは鈴木効果による時効硬化がヤング率の増加に寄与することを示した。

第5章「Mechanical properties and texture」では、結晶異方性と機械的特性の関係を調査している。ヤング率は圧延集合組織を有しているために面内異方性を呈する。時効熱処理を施すとヤング率は増加するが、集合組織の変化しておらず、CNCMの高ヤング率化にはひずみ時効硬化が有効であることを明らかにした。

第6章「Dislocation locking by Suzuki effect」では、時効熱処理前後のX線回折プロファイルのピークシフトからstacking fault probability を見積もり、熱処理で7倍増加することを示した。またひずみ振幅依存の内部摩擦を解析することで鈴木効果により、転位線がその全長に亘り固着される、転位の連続固着を生じていることを示した。

第7章「Thermal stability of microstructure in highly strained CNCM during aging」では、圧下率90％の冷間圧延を施したCNCMの加工組織の熱的安定性と鈴木効果との関係を調査した。鈴木効果が顕著な温度域で時効すると、強加工しているにもかかわらず転位密度の減少が緩やかであり、その過程で拡張転位が観察されることから鈴木効果が熱的安定性に寄与するということが示された。また、粒界への析出物の形成により鈴木効果が消滅することを示した。

第8章「Conclusion」では、本研究によって得られた知見をまとめた。

以上、精密機械用ばね材用の高品質Co-Ni-Cr-Mo合金は一般的な静的再結晶でも微細化が可能であり、ひずみ時効熱処理を施すことでより優れた機械的特性が得られる。また、CNCMの組織の熱的変化が鈴木効果で体系的に解釈できることを示した。

よって、本論文は博士（工学）の学位論文として合格と認める。